

Biodegradable and biocompatible inorganic–organic hybrid materials: 4. Effect of acid content and water content on the incorporation of aliphatic polyesters into silica by the sol-gel process

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Abstract

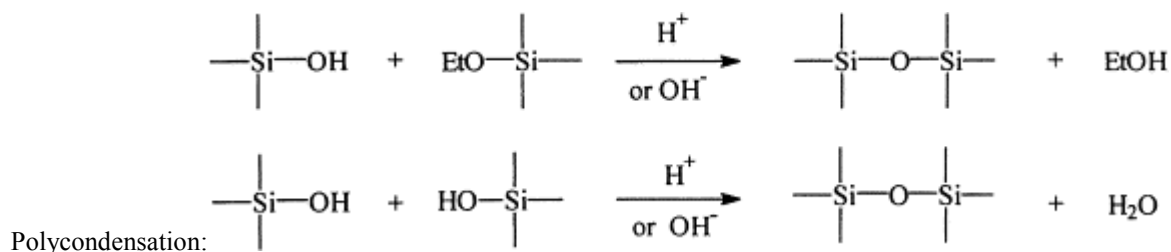
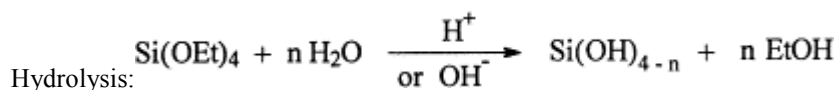
The extent of poly ϵ -caprolactone (PCL) incorporation into silica networks prepared by the sol-gel process depends on the HCl:tetraethoxysilane (TEOS) molar ratio and the H₂O:TEOS molar ratio, as well. The PCL incorporation increases with the concentration of the acid used as the catalyst. Dynamic mechanical analysis (DMA) indicates that increasing the acid concentration or decreasing the water content results in a higher glass transition temperature for the organic component in the hybrid materials, whereas the modulus does not change significantly. Small-angle X-ray scattering (SAXS) data agree with a nanoscopic phase separation of the two constitutive components: the organic polymer and the silica network. The characteristic length of this two-phase structure increases with acid content (except for the lower HCl:TEOS molar ratio of 0.05) and with water content (except for the higher H₂O:TEOS molar ratio of 2.0). The structure of the PCL/SiO₂ interface is mass fractal and the structure is more open when the acid content is lower or the water content higher.

Keywords: Nanocomposites; Sol-gel process; Inorganic–organic hybrid materials

1. Introduction

In the past decade, the area of inorganic–organic hybrid materials prepared by the sol-gel process has grown as a result of the potential of the new nanocomposites accordingly made available. These materials have the unique feature of combining the properties of traditional materials, i.e. ceramics and organic polymers, on the nanoscopic scale in sharp contrast to the macroscopic scale for traditional composites. As a rule, the general behaviour of these inorganic–organic nanocomposites is dependent on the nature and relative content of the constitutive inorganic and organic components, with a close dependence on the experimental conditions used for the implementation of the sol-gel reaction.

The sol-gel process can be basically schematized as a two-step network-forming process. Metal or silicon alkoxides, e.g. Si(OEt)₄, are hydrolyzed with the formation of intermediate species of the metal or silicon hydroxide type. These species then undergo a stepwise polycondensation with the formation of a metal or silicon oxide three-dimensional network.



Actually, hydrolysis and condensation are expected to occur simultaneously, so that the network forming process is controlled by a complex interplay of these two reactions.

As a variation of the traditional sol-gel process, an organic compound, e.g. an oligomer or a polymer, containing at least two groups reactive in the sol-gel process (preferably in terminal positions), can participate with the polycondensation reaction and be incorporated into new inorganic-organic hybrid materials. In these hybrids, inorganic and organic phases are intimately associated through covalent bonds. However, it has been shown that homogeneous and optically transparent hybrid materials can be obtained even in the absence of primary chemical bonding between an aliphatic polyester (poly ϵ -caprolactone; PCL) and silica, as a result of strong hydrogen-bonding interactions between the inorganic and organic phases [1].

As shown in the set of equations given above, the hydrolysis and polycondensation reactions are typically catalyzed by either an acid or a base, and water which is a reagent in the hydrolysis reaction, is also a by-product of the polycondensation reaction. This explains why the acidity and water content of the reactive system have an important role not only in the reaction kinetics but also in the structure of the final materials [2-5]. In addition to the basic effect of pH and water on the kinetics and thermodynamics of the sol-gel process, the addition of a polymeric reagent and the molecular characteristic features of this additive are also essential, e.g. the amount and molecular weight of the polymer, the difference in the solubility parameters of the polymer and the inorganic component, and the organic and water-soluble solvent(s) used for making the reaction medium homogeneous. All these parameters may affect the occurrence of the phase separation as the reaction progresses, and thus the structure and properties of the final material.

In previous papers, we have reported the synthesis and characterization of new biodegradable and biocompatible tetraethoxysilane-poly(ϵ -caprolactone) hybrid materials prepared by the sol-gel process, and particularly the study of property-structure-morphology relationships characteristic of these novel inorganic-organic composites [1 ; 6-8]. The purpose of this paper is to investigate how far the acid content (acid catalysis) and the water content control the incorporation of an aliphatic polyester (PCL) into silica.

We demonstrated that these new inorganic-organic hybrid materials are biomaterials endowed with 'bioactive' and resorbable properties, which pave the way to entirely new biomaterials that combine properties of classical materials, i.e. organic polymers and ceramics. This strategy has a potential in producing bone-bioerodible polymer composites for skeletal tissue repair [7].

2. Experimental section

2.1. Materials

Synthesis of α,ω -hydroxyl PCL ($M_n=2000$) was detailed elsewhere [1]. Tetraethoxysilane (Janssen), hydrochloric acid (12 N) (Lab Chemistry), tetrahydrofuran (Janssen), ethanol (Riedel-de Haen) were used as received.

2.2. Preparation of silica-poly(ϵ -caprolactone) hybrid materials

PCL/TEOS mixtures of various compositions were dissolved in THF (20 wt%) and hydrolyzed with a known amount of water with respect to the alkoxide functions. HCl was used as a catalyst in various HCl/TEOS molar ratios. In a representative synthesis, 1.5 g TEOS was added to the α,ω -triethoxysilane PCL (0.5 g, $M_n=2000$) solution in THF (10.0 ml) and thoroughly mixed until a homogeneous solution was formed. Deionized water (0.54 ml), ethanol (0.80 ml) and HCl (0.01 ml) were then added under rapid stirring at ambient temperature for ca. 10 min. This clear solution was cast into a plastic Petri dish and covered with a Parafilm. Based on a preliminary series of gelation experiments, the Parafilm has to be removed after several days depending on the PCL characteristics [14]. The gelified material was then dried under ambient conditions for 1 week prior to testing. These specific conditions were detailed elsewhere [1 ; 6] and proved to be efficient for preventing cracking phenomena from occurring. The usual film thickness was 0.1-1 mm.

2.3. Characterization

PCL was extracted from hybrid materials in a standard Soxhlet apparatus with THF, for at least 24 h until no further weight loss was observed. The sol fraction was calculated from the initial and the final weight of the samples. Dynamic Mechanical Analysis (DMA) was performed with a Dynamic Mechanical Analyzer (model 983, Du Pont Instruments) within the temperature range from -120 to 150°C with a heating rate of 3°C/min and a frequency of 0.5 Hz. Shear storage (G') and loss (G'') moduli (and $\tan \delta=G''/G'$) were calculated from the phase

shift (δ) at the 0.5 Hz frequency. The typical size of the samples used was 25 mm×0.15 mm×5 mm. Although the samples were clamped over a short gauge length, the clamping arrangements were such that measurement of the true shear moduli could not be ascertained. Small-angle X-ray scattering (SAXS) measurements were carried out at the 'Laboratoire pour l'Utilisation du Rayonnement Electromagnetique' (LURE; Orsay France) on DCI (D24 station). The size of the X-ray beam ($\lambda=1.488 \text{ \AA}$) at the sample was smaller than 1 mm^2 , so that no desmearing of the data was required. The scattered X-rays were detected with a Argon–CO₂ gas-filled, one-dimensional position-sensitive detector (with a resolution of 0.4444 mm). The sample-to-detector distance (1151 mm) allowed SAXS data to be recorded in the 0.02–0.8 nm⁻¹ s range. These data were plotted as relative intensity versus s after correction for parasitic scattering and sample absorption. The background scattering was corrected in the standard manner.

3. Results and discussion

Although the acidity and water content are known for a decisive effect on the fate of the sol-gel process [2-5], their role has not been thoroughly analyzed in the specific case of hybrid materials and their final structure. This is the reason why a systematic study has been undertaken on the property–structure relationships of PCL/silica hybrid materials in relation to the acid and water contents of the reaction mixture. All the prepared samples (Table 1) were transparent, suggesting that no phase separation between the organic and the inorganic components was detectable on the scale of the visible light wavelength. As a rule, the gelation kinetics decreases with acid content, i.e. the HCl:TEOS molar ratio. The effect of the water content, thus the H₂O:TEOS molar ratio, is more complex since the gelation progress goes through a minimum when the H₂O:TEOS ratio is increased from 0.25 up to 2.0 at a constant HCl:TEOS ratio of 0.05 (Table 1). This dependence has been confirmed by repeating the preparation and characterization of samples, e, f, a and g.

Table 1. Main characteristics of the PCL ($M_n=2000$)/silica hybrid materials synthesized in this study

Samples	HCl:TEOS (mol. ratio)	H ₂ O:TEOS (mol. ratio)	PCL wt% (theor.) ^a	PCL wt% ^b Curing conditions		
				at 25°C	100°C for 1 day	100°C for 2 days
a	0.05	1.0	46.5%	9.0% (19.4%)	34.0% (73.1%)	35.0% (75.3%)
b	0.10	1.0	46.5%	15.5% (33.3%)	43.5% (93.5%)	46.5% (100%)
c	0.20	1.0	46.5%	23.0% (49.5%)	46.5% (100%)	46.5% (100%)
d	0.50	1.0	46.5%	23.0% (49.5%)	46.5% (100%)	46.5% (100%)
e	0.05	0.25	46.5%	9.5% (20.4%)	38.0% (81.7%)	37.5% (80.6%)
f	0.05	0.5	46.5%	9.5% (20.4%)	33.0% (71.0%)	34.0% (73.1%)
g	0.05	2.0	46.5%	17.0% (36.6%)	37.5% (80.6%)	36.5% (78.5%)

It must be noted that when the water content is too high, i.e. when H₂O:TEOS exceeds 2, the original reaction mixture is a two-phase system, at least for the THF/ethanol solvent mixture (i.e. 100:8, v:v) used in this work, which results in an opaque final product.

3.1. Extent of the PCL incorporation into the silica network

In order to know to which extent PCL has been incorporated into the silica network, this polymer has been selectively extracted with THF in a Soxhlet apparatus. As previously reported, a decrease in PCL content and an increase in PCL molecular weight, number of functional groups per chain and curing temperature (i.e. 100°C) have a favourable effect on PCL incorporation [1]. In this work, all the experimental conditions were kept the same except for the acid and water contents which were systematically changed (Table 1).

Table 1 shows that increasing the acid content has a very beneficial effect on PCL incorporation. For example, the fraction of PCL incorporated in the series of samples a–d increases from 9.0% up to 23.0% when the HCl:TEOS molar ratio is increased from 0.05 to 0.5. However, when the acid content is high enough, i.e. HCl:TEOS \geq 0.20, any further increase has no significant effect anymore (samples c and d in Table 1). Clearly, the sample annealing at 100°C has a very beneficial effect on the PCL conversion. Indeed, when the higher beneficial HCl:TEOS ratio is used (\geq 0.20), PCL is completely incorporated into the silica network for a 1 day curing at 100°C.

In reference to a previous work by Aelion et al., the hydrolysis rate constant of TEOS in different solvents increases linearly with the H^+ or H_3O^+ concentration [9]. However, as long as the rate determining step in the sol-gel process is unknown, it is not possible to decide whether the acid catalysis has a decisive effect on the hydrolysis reaction rather than on the polycondensation one.

When the HCl content is kept constant, PCL conversion is higher for intermediate water contents ($H_2O:TEOS=0.5-1.0$) as shown by the series of samples a, e, f and g in Table 1. Indeed, PCL incorporation yield for a 1 day curing at $100^\circ C$ is higher in sample e (81.7%, $H_2O:TEOS=0.25$) and sample g (80.6%, $H_2O:TEOS=2.0$) compared to sample f (71.0%, $H_2O:TEOS=0.5$) and sample a (73.1%, $H_2O:TEOS=1.0$). Once again, curing at $100^\circ C$ (for 1 day) has a beneficial effect on the PCL conversion, although a longer annealing time at this temperature, i.e. 2 days, is not convincingly beneficial to the PCL conversion (Table 1).

The explanation for the effect of the water content on PCL incorporation is not straightforward. Indeed, as a reagent of the hydrolysis reaction, water must have a kinetic effect on this reaction. For instance, Aelion et al. reported that an increase in the $H_2O:TEOS$ molar ratio from 1.86 to 3.72 was responsible for an increase in the rate constant for the TEOS hydrolysis from 0.042 to $0.059 \text{ l mol}^{-1} \text{ s}^{-1} [\text{acid}]^{-1}$ [9]. However, Schmidt et al. observed a slowing down of the TEOS hydrolysis when the $H_2O:TEOS$ molar ratio was increased from 0.5 to 2 [10]. These authors explained this effect by the 'special experimental conditions and the water acting as a proton acceptor which decreases the proton activity' [11]. Last but not least, the water content controls in this study the PCL solubility and thus the occurrence of a more or less rapid phase separation in the reaction medium. This phenomenon must also influence the progress of the whole reaction and contribute to the complexity of the hybrid network formation.

3.2. Dynamic mechanical analysis

Fig. 1 shows the effect of the water content on the dynamic mechanical properties of SiO_2 -PCL hybrid materials at a constant acid content ($HCl:TEOS=0.05$). In the low temperature range, the shear storage modulus of all the samples has a plateau value of ca. $9.5 \times 10^9 \text{ Pa}$. As the temperature is increased beyond $-50^\circ C$, G' decreases by half an order of magnitude over a broad temperature range. The temperature dependence of $\tan \delta$ confirms a broad relaxation assigned to the glass transition temperature of the PCL phase. This observation is evidence for a microphase separation in all these transparent hybrid materials. The temperature at the maximum of this relaxation is found to increase from -15 to $-6^\circ C$ when the water content ($H_2O:TEOS$) is decreased from 1 to 0.25. A previous paper has reported that the mobility of PCL was restricted when this polymer was part of the ceramer, in agreement with a shift of the glass transition temperature to higher temperatures [8]. From this study, it thus appears that the loss in the PCL chain mobility is more important than the water content of the reaction mixture. A broad loss peak of a low intensity is observed at ca. $-80^\circ C$ for all the samples. It might be tentatively assigned to the β relaxation of the PCL phase.

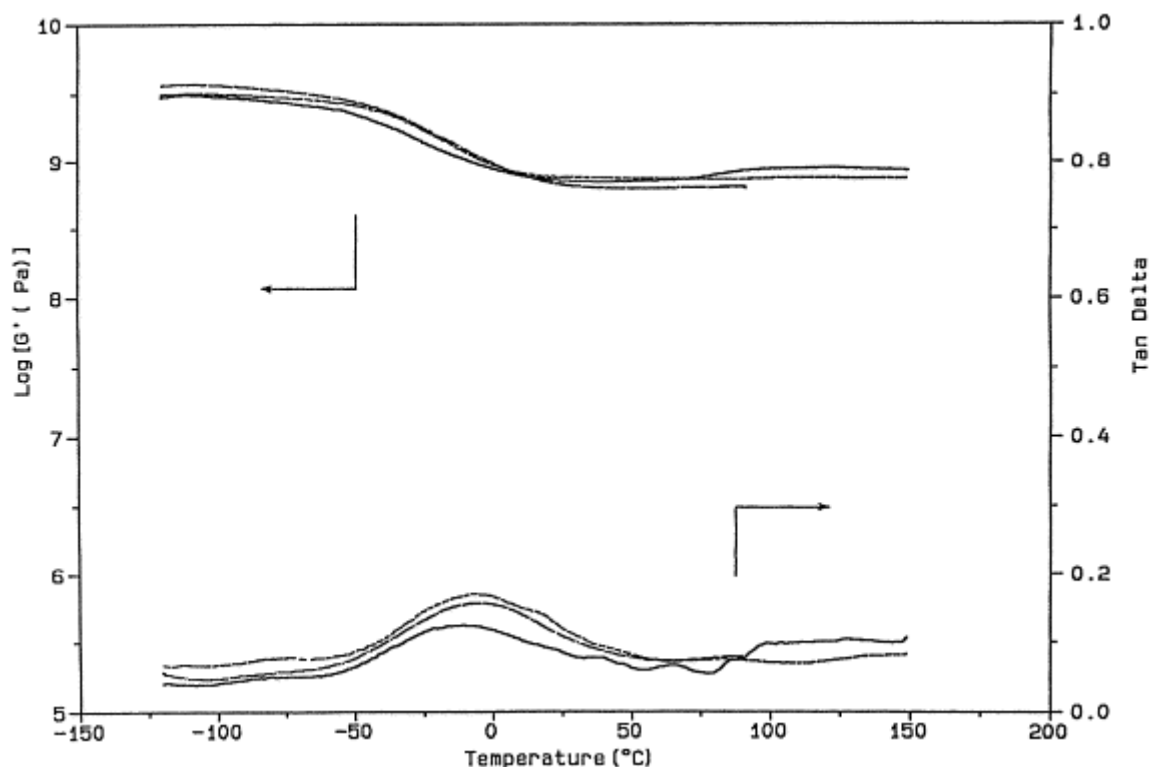


Fig. 1. Dynamic mechanical analysis of hybrid materials prepared from 80 wt% TEOS, 20 wt% α,ω -hydroxyl PCL ($M_n=2000$), HCl:TEOS=0.05, and various water contents: H₂O:TEOS (mol:mol)=1.0 (—), 0.5 (- - -) and 0.25 (- · -).

The effect of the acid content on the dynamic mechanical properties at a constant water content (H₂O:TEOS=1.0) has also been investigated. The same curves as in Fig. 1 are observed, thus a small and broad relaxation at ca. -80°C, followed by the glass transition of PCL at higher temperatures. No significant effect of the acid content on the shear storage modulus can be detected. The glass transition temperature of PCL is found to slightly increase from -15 to -7.5°C as the acid content (HCl:TEOS) is increased from 0.05 to 0.50, all the other conditions being the same. Actually, there is a parallelism between the extent of the PCL incorporation into the silica network (Table 1) and the restricted mobility of these chains in a close dependence on the acid catalysis of the sol-gel reaction. Indeed, when more acid is used, the reaction is not only more complete, but also faster accounting for a less extended PCL-silica phase separation and thus more constraints on the mobility of the PCL chains.

The same qualitative relationship between PCL incorporation and PCL mobility in the hybrid materials in relation to the water content is no longer as straightforward as in the case of the acid content, possibly in line with the more complex role of water compared to that of the acid.

3.3. Small-angle X-ray scattering (SAXS)

In order to probe the phase structure of the PCL-silica ceramers, SAXS experiments have been carried out. Typical SAXS profiles are shown in Fig. 2 and Fig. 3, parts A, where the scattered intensity (I) is plotted against the scattering vector, s , which is defined as $2 \sin \theta / \lambda$, where θ is half the radial scattering angle (or the internal scattering angle) and λ is the wavelength of the X-ray beam. A log-log plot of the SAXS intensity versus the scattering vector, s , is shown in Fig. 2 and Fig. 3, parts B. The analysis of the limiting power law in the Porod region of the scattering curves can provide some information on the PCL-silica interface. Indeed, in the case of fractal structures, the SAXS intensity $I(s)$ agrees with the following power laws [12]:

$$\text{mass fractal } I(s) \sim s^{-D_m}, \quad 1 < D_m < 3$$

$$\text{surface fractal } I(s) \sim s^{-(6-D_s)}, \quad 3 < 6-D_s < 4$$

where D_m is the mass fractal dimension and D_s is the surface fractal dimension.

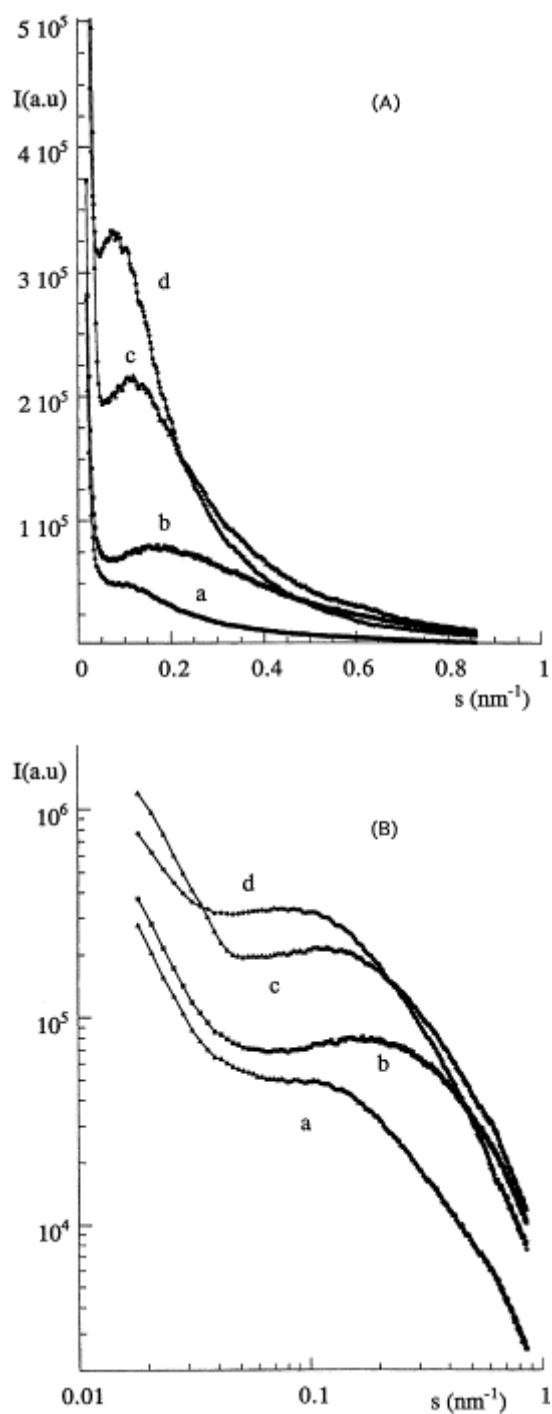


Fig. 2. (A) SAXS profiles for hybrid materials prepared from 80 wt%, 20 wt% α,ω -hydroxyl PCL ($M_n=2000$), and various acid contents: HCl:TEOS (mol:mol)=0.05 (a), 0.10 (b), 0.20 (c) and 0.50 (d). (B) Log-log plots of the SAXS intensity versus the scattering vector s for the same samples.

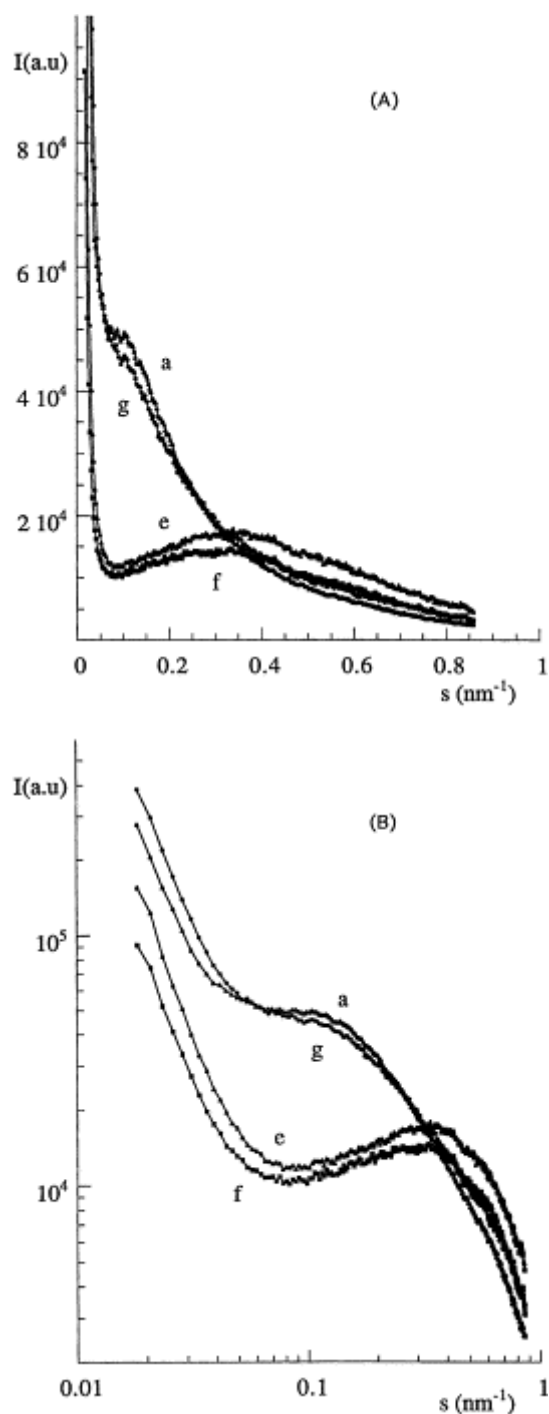


Fig. 3. (A) SAXS profiles for hybrid materials prepared from 80 wt%, 20 wt% α,ω -hydroxyl PCL ($M_n=2000$), and various water contents: $H_2O:TEOS=1.0$ (a), 0.50 (f), 0.25 (e) and 2.0 (g). (B) Log-log plots of the SAXS intensity versus the scattering vector s for the same samples.

As shown in Fig. 2A, a scattering maximum is observed in the SAXS profiles of the hybrid materials. A periodic fluctuation in the electron density is thus responsible for a 'correlation length' (ζ) in the system, in agreement with a microscopic phase separation between PCL and silica. This 'correlation length' has been calculated as the reverse of the scattering parameter s at which the maximum is observed. Conversely, the fractal dimension (D) has been calculated from the limiting slope of the scattering profile (Fig. 2 and Fig. 3, parts B). All these data are listed in Table 2.

Table 2. Correlation length (ζ) and fractal dimension (D) for a series of PCL–silica hybrid materials

Samples	a	b	c	d	e	f	g
HCl:TEOS (mol. ratio)	0.05	0.10	0.20	0.50	0.05	0.05	0.05
H ₂ O:TEOS (mol. ratio)	1.0	1.0	1.0	1.0	0.25	0.50	2.0
ζ (nm)	9.5	5.9	8.3	12.5	2.9	3.3	8.3
D	1.6	1.6	1.8	2.0	—	—	1.4

The weight composition of the PCL–silica hybrid materials prepared in this study is close to 50%. The co-continuity of the PCL and silica phases has been previously reported in this composition range [8]. The average distance between the constitutive components (characteristic length) is of a few nanometers, and increases with the acid content except for the lower HCl:TEOS ratio (sample a).

In the traditional sol-gel process based on the hydrolysis and polycondensation of TEOS, 'polymeric' silicon alkoxide can grow by reaction-limited cluster–cluster aggregation (RLCCA) in dilute acidic solutions [13-15]. All the collisions are not effective in forming covalent bonding, and the fractal dimension (D) is typically 2.0–2.1 for a RLCCA mechanism. If the silicon alkoxide clusters are permanently attached upon first contact, the so-called diffusion-limited cluster–cluster aggregation (DLCCA) [13-14] leads to slightly more open structures with $D=1.8$. In the case of the TEOS–PCL system studied in this work, the TEOS polycondensation also occurs in dilute acidic solution, so that a fractal dimension intermediate between the values predicted for the two aggregation models (i.e. RLCCA and DLCCA) would be reasonable. Clearly, the limiting slope for all the analyzed samples is less than 2.0, which indicates that the interface structure is mass fractal whatever the acid content, in agreement with a co-continuous two-phase structure. It also appears that the fractal dimension increases with acid content (Table 2), which suggests that more open structures are formed when the acid content is decreased. As previously pointed out, the hydrogen bonding between PCL and silica must have a retardation effect on their phase separation [8] and thus perturb the aggregation of the inorganic constitutive component, which can account for a fractal dimension smaller than expected for neat TEOS under acidic conditions.

A scattering maximum is also observed in the SAXS profile of PCL–silica hybrid materials prepared from various H₂O:TEOS molar ratios (Fig. 3A). Fig. 3A shows that the electronic density fluctuations decrease with the H₂O:TEOS molar ratio, which agrees with the less extended phase separation suggested by DMA. As shown in Table 2, ζ passes through a maximum when the H₂O:TEOS molar ratio is increased from 0.25 to 2.0. Fractal dimensions have also been calculated from Fig. 3B, except for the samples e and f, because the power law $I(s) \sim s^{-D}$ is not observed over a large enough range. The interface structure for the samples a and g is mass fractal ($1 < D < 3$), consistently with a co-continuous two-phase morphology, although more open structures are formed at the higher H₂O:TEOS ratio (2.0), the HCl:TEOS ratio being constant (0.05).

In all the correlations discussed in this paper, the data for sample a are singular, since they correspond to a maximum or a minimum. Although this characteristic behaviour is reproducible (e.g. the error on data in Table 1 is 0.2%), the reason for it is still unclear.

4. Conclusion

The extent of the PCL incorporation into the silica network formed by the sol-gel process depends on the HCl:TEOS molar ratio and the H₂O:TEOS one. Curing at 100°C is favourable to the PCL incorporation and increasing acidity, as well. At HCl:TEOS molar ratios higher than 0.20, the PCL incorporation is complete for a 1 day curing at 100°C. When the HCl:TEOS ratio is kept constant (e.g. HCl:TEOS=0.05), the PCL incorporation passes through a minimum when the H₂O:TEOS ratio is increased from 0.25 to 2.0. According to dynamic mechanical analysis, an increased acidity results in a higher glass transition temperature (T_g) for the organic component (PCL) of the hybrid materials. Conversely, at a constant HCl:TEOS ratio of 1.0, T_g of PCL is found to decrease when the H₂O:TEOS molar ratio is increased (from 0.25 to 1.0). SAXS measurements conclude to a correlation length, which increases with the HCl:TEOS molar ratio (from 0.10 to 0.50), and passes through a minimum when the H₂O:TEOS ratio is increased (from 0.25 to 1.0). The analysis of the Porod region of the SAXS profiles confirms that the PCL–SiO₂ interface is mass fractal, in agreement with a co-continuous two-phase morphology. More open structures are, however, formed at lower acid content and higher water content, respectively.

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